Adsorption (2009) 15: 381–389
DOI 10.1007/s10450-009-9155-z

Adsorption study for removal of Congo red anionic dye using organo-attapulgite

H. Chen · J. Zhao

Received: 5 July 2008 / Revised: 12 January 2009 / Accepted: 9 February 2009 / Published online: 20 February 2009

Abstract The organo-attapulgite was prepared using hexadecyltrimethylammonium bromide (HTMAB) with equation equivalent ratio of HTMAB to CEC of attapulgite added and then used as adsorbent for the removal of Congo red (CR) anionic dye from aqueous solution. Adsorbent characterizations were investigated using infrared spectroscopy and X-ray diffraction. The effects of contact time, temperature, pH and initial dye concentration on organo-attapulgite adsorption for CR were investigated. The results show that the amount adsorbed of CR on the organo-attapulgite increase with increasing dye concentration, temperature, and by decreasing pH. The adsorption kinetics was studied with the pseudo-first-order, pseudo-second-order and intraparticle diffusion models, and the rate constants were evaluated. It was found that the adsorption mechanisms in the dye/organo-attapulgite system follow pseudo-second-order kinetics with a significant contribution of film diffusion. Equilibrium data fitted perfectly with Langmuir isotherm model compared to Freundlich isotherm model, and the maximum adsorption capacity was 189.39 $\mathrm{mg\,g^{-1}}$ for the adsorbent. Kinetic and desorption studies both suggest that chemisorption should be the major mode of CR removal by the organo-attapulgite. The results indicate that HTMAB-modified attapulgite could be employed as low-cost material for the removal of Congo red anionic dye from wastewater.

Keywords Organo-attapulgite · Congo red · Adsorption · Kinetics · Isotherms · Desorption

---

H. Chen (✉) · J. Zhao
School of Pharmaceutical and Chemical Engineering, Taizhou University, Linhai, People's Republic of China
e-mail: chenhao2212@sohu.com

1 Introduction

Nowadays the large amounts of dyes can be synthesized and used for many industries such as textiles, paper, leather, plastics, etc. (Chiou et al. 2004). The colored effluents of waste water from these industries can be mixed in surface water and ground water systems, and then they may also transfer to drinking water and bring a chief threat to human health due to either toxic or mutagenic and carcinogenic for most of dyes (Gong et al. 2005). Therefore, it is necessary to remove the dye pollutions. However, dyes usually have a synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegradate and photodegradate (Seshadri et al. 1994), it bring some difficulties for the treatment of these pollutants. Hence, it is imperative that a suitable treatment method should be devised.

In recent years, many methods including chemical oxidation (Neamtu et al. 2004), reverse osmosis (Gupta et al. 1990), coagulation and flocculation (Halliday and Beszedits 1986), biological treatments (Patil and Shinde 1988), photodegradation (Wahi et al. 2005), and adsorption (Rao and Rao 2006), have been developed for treating dye containing wastewater. Among these methods, adsorption is known to be a promising technique due to the ease of operation and comparable low cost of application in decoloration process. Although activated carbons have been most widely used for the adsorption of dyes (Rao and Ashutosh 1994; Pelekani and Snoeyink 2001; Lorenc-Grabowska and Gryglewicz 2007), clay minerals have been increasingly gaining attention because they are cheaper than activated carbons and they usually have chemical and mechanical stability, high surface area and structural properties. Many workers have employed clay minerals such as bentonite (Tahir and Rauf 2006; Hu et al. 2006), montmorillonite (Wang et al.

2004), smectite (Ogawa et al. 1996; Czímerová et al. 2004), kaolinite (Harris et al. 2001), sepiolite (Alkan et al. 2004, 2005; Özcan et al. 2004, 2006), and zeolite (Armağan et al. 2004), etc. for removing the dyes from wastewater. It can be found in above literature that adsorption capacity of clays is commonly high for cationic dyes, whereas a low adsorption capacity was obtained for anionic dyes. The reason for this case is that the clay's surface is usually negatively charged due to the isomorphic substitutions, which is not benefit to adsorb anions. Hence, the surface of the natural clays has to be modified in a manner to improve their adsorption capacities for anionic dyes.

Attapulgite is a crystalline hydrated magnesium silicate with a fibrous morphology having the formula $(Mg,Al)_2Si_4O_{10}(OH)\cdot 4(H_2O)$ which is also known as palygorskite or fuller's earth. It possesses large specific surface area and moderate cation exchange capacity, which is beneficial for the adsorption of many pollutants such as heavy metals and dyes from wastewater (Chen and Wang 2007; Chen et al. 2007; Mckay et al. 1985; Al-Futaisi et al. 2007). There is much information on the removal of dyes by attapulgite (Mckay et al. 1985; Al-Futaisi et al. 2007). Mckay et al. (1985) selected fuller's earth as adsorbent to adsorb a basic dye (Astrazone Blue—Basic Blue 69) and an acidic dye (Telon Blue—Acid Blue 25). The result presented that the equilibrium saturation adsorption capacities were 1200 mg dye g^{-1} Fuller's earth and 220 mg dye g^{-1} Fuller's earth for Astrazone Blue and Telon Blue, respectively. Al-Futaisi et al. (2007) reported the adsorption of methylene blue (MB) basic dye by attapulgite. The results showed that attapulgite clay can uptake up to 51 mg of MB per 1 g mass of clay. MB adsorption is best fitted by Langmuir isotherm, and a pseudo-second-order kinetic model can be efficiently used to predict the kinetic of adsorption of MB by the attapulgite.

Recently, organoclay has been paid more and more attention due to the novel properties compared with natural clay (de Paiva et al. 2008). There are many negative charges on the surface of attapulgite due to the isomorphic substitutions of Al^{3+} for Si^{4+} in the tetrahedral sheets and Mg^{2+} for Al^{3+} in the octahedral sheets. Such negative charges are balanced by the presence of exchangeable cations (Na^+, Ca^{2+}, etc.) in the lattice structure (Galan 1996). So, it can be modified by organic cations such as quaternary ammonium compounds by ion exchange reaction. Huang et al. (2007) have studied adsorption of a water soluble dye, Reactive Red MF-3B, using octodecyl trimethyl ammonium chloride modified attapulgite clay and found that, the surfactant-modified clay could be a good adsorbent for treating Reactive Red MF-3B-contaminated waters. Despite the fact that surfactant-modified attapulgite clay has been reported to select as adsorbent for the removal of anions dye reactive red MF-3B, there have been no studies on adsorption characteristic of organo-attapulgite modified by hexadecyltrimethylammonium bromide (HTMAB) for anionic dyes such as a common one, Congo red.

The main objective of this investigation was to examine adsorption characteristic for Congo red anionic dye on HTMAB-modified attapulgite. The effect of such factors as pH, contact time, initial concentration and temperature was investigated. The adsorption kinetics and desorption were also studied.

2 Materials and methods

2.1 Materials

The attapulgite clay was obtained from Xuyi Aotebang Co. (Jiangsu, China). The sample was ground and sieved to 200 mesh size. Chemical analysis of the sample was performed in the PANalytical Company with an Magix PW 2403 XRF Spectrometer and the result is given in Table 1. The cation exchange capacity (CEC) of the attapulgite clay was determined using the ammonium acetate method (Bache 1976) and it was calculated to be 37.7 meq/100 g. Congo red (CR) was obtained from Tianjin Kermel Chemical Co. (Tianjin, China) and used as received. The chemical structure of CR is shown in Fig. 1. Hexadecyltrimethylammonium bromide (HTMAB) was purchased from Shanghai Reagent Co. (Shanghai, China) as high purity (>99%) product. All of

Table 1 Chemical composition of attapulgite sample

Component	Weight (%)
SiO_2	66.43
MgO	13.52
Al_2O_3	10.25
Fe_2O_3	5.51
CaO	1.82
TiO_2	0.53
MnO	0.32
K_2O	1.12
Na_2O	0.11
P_2O_5	0.26
SO_3	0.02

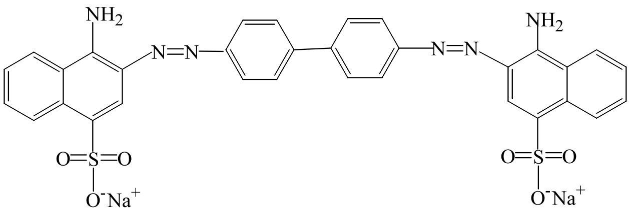

Fig. 1 Chemical structure of Congo red

chemicals other used were of analytical grade. In all experiments distilled water was employed.

2.2 Preparation of organo-attapulgite

The organo-attapulgite was prepared by the cation exchange reaction. 10 g of attapulgite was mixed in 100 ml HTMAB aqueous solution containing the amount of surfactant equivalent ratios to 1.0 of CEC of attapulgite. The suspension was stirred at room temperature for 24 h. The mixture was filtered and washed several times with distilled water until no bromide ion was detected by $AgNO_3$ solution ($0.1\ \mathrm{mol\,L^{-1}}$). The sample was dried in an air oven at 105 °C and ground to 200 mesh size.

2.3 Characterization of samples

Infrared spectroscopic measurements were done on a Thermo Nicolet NEXUS TM spectrophotometer using the KBr pellets method. The spectrum was collected 32 times and corrected for the background noise. The X-ray diffractograms were obtained on a X'pert PRO diffractometer with working conditions CuKα, 30 mA and 40 kV ($\lambda = 1.54060$ Å). The scanning was made at room temperature between 5 and 25 ° in 2θ with a step size of 0.02 °.

2.4 Adsorption experiments

Adsorption measurements were determined by batch experiment of 50 mg of the sample with 25 ml of aqueous dye solutions. The pH of dye solution was adjusted with dilute HCl or NaOH solution by using a Mettler Toledo 320 pH meter. The mixture was shaken in a thermostatic shaker bath (THZ-98A) at 120 rpm and a given temperature. The pH 6.0 of suspension and 30 °C were selected except for the study about effects of pH and temperature, respectively. After a shaking time was completed, the suspension was centrifuged at 5000 rpm for 10 min. The equilibrium concentration of dye solution was measured using UV-Vis spectrophotometer (Specord 200) at the $\lambda_{\max}$ value of 500 nm for CR. The amount of the dye adsorbed onto natural, and organo-attapulgite were determined by the difference between the initial and remaining concentration of dye solution. The adsorption capacity of CR on adsorbent was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

where q_e is the amount of CR adsorbed on adsorbent ($\mathrm{mg\,g^{-1}}$), C_0, the initial concentration of CR solution ($\mathrm{mg\,L^{-1}}$), C_e, the equilibrium concentration of CR solution ($\mathrm{mg\,L^{-1}}$), m, the mass of adsorbent used (g) and V, the volume of CR solution (L). The experiments were carried out by varying pH of dye solution (4–9), initial dye concentration (200–600 $\mathrm{mg\,L^{-1}}$), contact time (0–150 min) and temperature (30, 40 and 50 °C).

2.5 Desorption studies

For batch desorption study, 50 mg of the adsorbent utilized for the adsorption of an initial dye concentration of 500 $\mathrm{mg\,L^{-1}}$ was separated from the dye solution by centrifugation. The dye-loaded adsorbent was washed gently with water to remove any unadsorbed dye. Then the spent adsorbent was stirred using a magnetic stirrer with 25 ml of neutral distilled water, 0.1 $\mathrm{mol\,L^{-1}}$ NaOH solution for 6 h, in turn. The desorbed dye was determined as mentioned before.

3 Results and discussion

3.1 Characterization of the adsorbents

3.1.1 FT-IR analysis

The FT-IR spectra of attapulgite and organo-attapulgite are shown in Fig. 2. Compared to spectra of attapulgite, those of organo-attapulgites show the strong absorption bands at 2930 and 2856 $\mathrm{cm^{-1}}$, which indicate –CH_3 and –CH_2 groups. In addition, the absorption band at 1650 $\mathrm{cm^{-1}}$ is attributed to the –OH bend vibration of water (Frost et al. 2001), which becomes weaker with the increase of added amount of HTMAB. It indicates surface property of attapulgite become more hydrophobic via surfactant modification. The above variations in FT-IR spectra suggest that natural attapulgite has been modified by surfactant and surface property of attapulgite has been changed evidently.

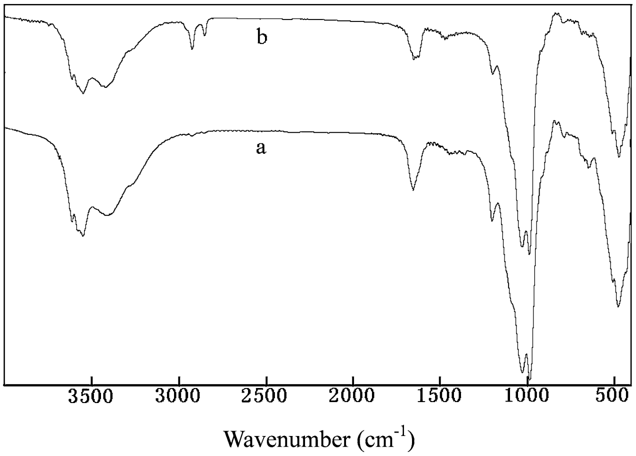

Fig. 2 FT-IR spectra of attapulgite (**a**) and organo-attapulgite (**b**)

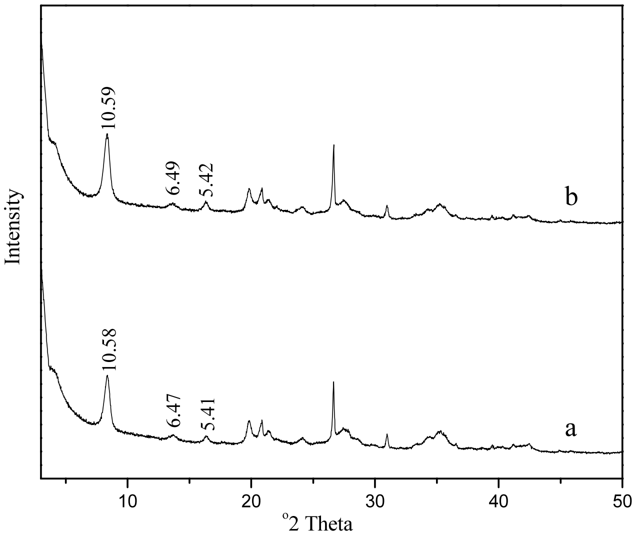

Fig. 3 X-ray diffraction patterns of attapulgite (**a**) and organo-attapulgite (**b**)

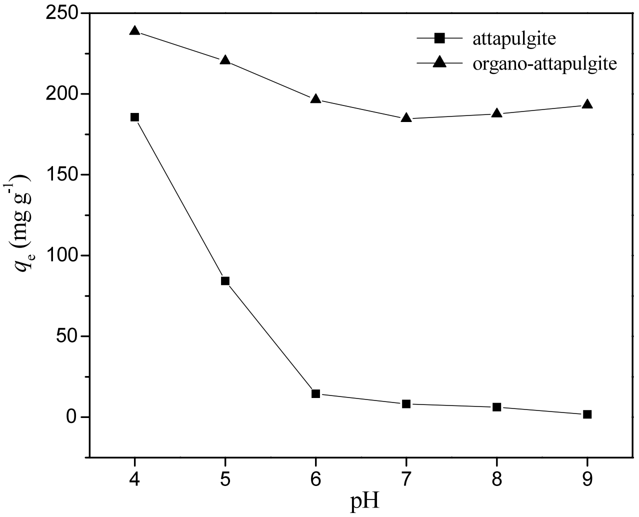

Fig. 4 Effect of pH for the adsorption of CR onto attapulgite and organo-attapulgite (the initial dye concentration: 500 mg L^{-1}; temperature: 30 °C; equilibrium time: 2 h)

3.1.2 XRD analysis

The XRD patterns of attapulgite and organoclay are shown in Fig. 3. It was observed that attapulgite was the main component phase in the clay used in this study, with appreciable amounts of smectite, quartz and calcite. The characteristic *d* spacing corresponding to (010), (200) and (130) reflections of attapulgite were 10.58, 6.47, and 5.41 Å, respectively. After organification with HTMAB, all of the above *d* spacing for the attapulgite has almost no change. According to the results of XRD and FTIR, it can be concluded that the crystal structure of the attapulgite is maintained and the surfactant is only adsorbed on the surface of attapulgite needles and no HDTMA cations were intercalate into the interlayer of attapulgite.

3.2 Effect of pH

The pH of the dye solution is an important parameter controlling the adsorption capacity of dye onto clay (Wang et al. 2005). Figure 4 shows the adsorption capacity for natural attapulgite and organo-attapulgite at different pH of initial CR solution. It can be observed that the adsorption capacity of the two adsorbents decrease with an increase in pH of the initial solution from 4 to 6, and then reach gradually constant as the pH become neutral and more basic. The difference of the trend in pH vs. adsorption capacity is that the adsorption is highly dependent on pH of the solution for natural attapulgite compared to the organo-attapulgites, which can be interpreted in terms of electronegative property of attapulgite surface. As pH value is low (4.0), the negatively charged sites (Si–O$^-$) and silanol groups (Si–OH) on attapulgite are more protonated and form Si–OH$_2^+$, hence, they are more available to adsorb CR through the electrostatic attraction. Consequently, high adsorption capacity of CR on adsorbent occurs. As pH increases to 6.0, the attapulgite surface at the moment becomes negatively charged as a whole. A negative charged surface site on the clay does not favor the adsorption of anionic dye due to electrostatic repulsion and causing an evident decrease in the CR adsorption. Since adsorption sites of attapulgite surface is replaced partly by surfactant molecules by cation exchange reaction, magnitude of variable negatively charged sites depended on pH decrease and consequently the adsorption capacity decreases slowly with the increase in pH. It is worthy to note that still significant amount of dye removal onto organo-attapulgites was observed as the pH of the solution increases from 7 to 9. This suggests that the other mechanism not electrostatic attraction may be operative (Baskaralingam et al. 2006).

3.3 Effect of initial dye concentration, contact time and temperature

The effect of dye concentration and contact time on the removal of CR by organo-attapulgite at the pH value of 7.0 and 30 °C are shown in Fig. 5. The dye concentration used in this study was 250, 300 and 350 mg L^{-1} for the adsorbent. As seen in Fig. 5, the equilibrium adsorption capacity of the adsorbent for CR increases with increasing initial dye concentration. Namely, the more concentrated the dye solution, the higher the adsorption capacity. This is probably due to a high driving force for mass transfer in high dye concentration. It is also observed from the graphs that the adsorption of CR is rapid from the beginning of the experiment and thereafter it proceeds at a slower rate and finally reaches to equilibrium. All the data after about 90 min are essentially at

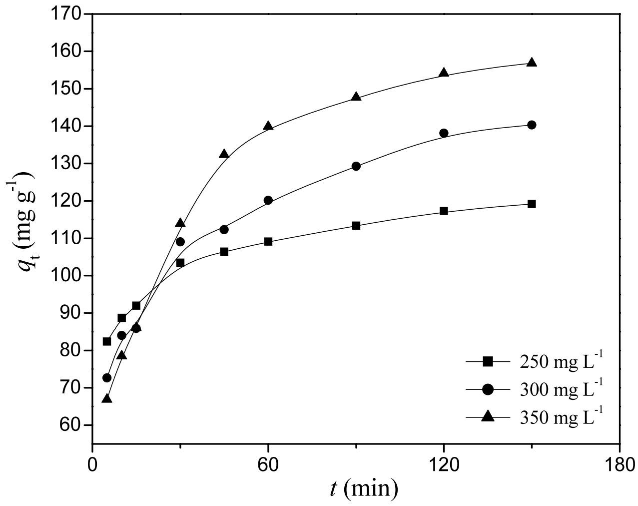

Fig. 5 Effect of initial dye concentration and contact time for the adsorption of CR onto organo-attapulgite

equilibrium. Based on the above results, 120 min was fixed as equilibrium time throughout this study.

The effect of temperature on the equilibrium adsorption capacity of CR onto organo-attapulgite was investigated at a concentration of 500 $\mathrm{mg\,L^{-1}}$ and the result showed the equilibrium adsorption capacities were 184.77, 201.36 and 209.75 $\mathrm{mg\,g^{-1}}$ at 30, 40 and 50 °C, respectively. It is clearly seen that the equilibrium adsorption capacity increases with increasing temperature from 30 to 50 °C, which indicates the increase in the mobility of large dye molecules with increasing temperatures. The result implies that chemical adsorption mechanism may play an important role in this system (Aksu 2002).

3.4 Adsorption kinetics

In order to examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, pseudo first-order, pseudo second-order and intraparticle diffusion kinetic equations were used to test the experimental data. The pseudo-first-order kinetic model was suggested by Lagergren (1898) for the adsorption of solid/liquid systems and its formula is given as:

$$\frac{dq_e}{dt} = k_1(q_e - q_t). \tag{2}$$

After integration with the initial condition $q_t = 0$ at $t = 0$, (3) can be obtained

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{3}$$

where q_t is the adsorption capacity at time t ($\mathrm{mg\,g^{-1}}$) and k_1 ($\mathrm{min^{-1}}$) is the rate constant of the pseudo-first adsorption, was applied to the present study of dye adsorption. The rate constant, k_1 and correlation coefficients of the dye under different concentrations were calculated from the linear plots of $\log(q_e - q_t)$ versus t (figure not shown) and listed in Table 2. The correlation coefficients for the pseudo first-order kinetic model are low. Moreover, a large difference of equilibrium adsorption capacity (q_e) between the experiment and calculation was observed, indicating a poor pseudo first-order fit to the experimental data.

The kinetic data were further analyzed using Ho's pseudo-second-order kinetics model. This model is based on the assumption the sorption follows second order chemisorption. It can be expressed as (Ho and McKay 1999):

$$\frac{dq_e}{dt} = k_2(q_e - q_t)^2. \tag{4}$$

When the initial condition is $q_t = 0$ at $t = 0$, integration leads to (5):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where k_2 ($\mathrm{g\,mg^{-1}\,min^{-1}}$) is the rate constant of the pseudo-second-order adsorption. The rate constant k_2, the q_e value and the corresponding linear regression correlation coefficient r^2 under different concentrations were calculated from the linear plots of t/q_t against t (figure not shown) and given in Table 2. At all studied initial dye concentrations, the straight lines with extremely high correlation coefficients (>0.999) were obtained. In addition, the calculated q_e values also agree with the experimental data in the case of pseudo-second-order kinetics. These suggest that the adsorption data are well represented by pseudo-second order kinetics and the supports the assumption (Ho and McKay 1999) that the rate-limiting step of CR onto organo-attapulgite may be chemical sorption or chemisorption. From Table 2, the values of the rate constant k_2 decrease with increasing initial dye concentration for the organo-attapulgite. The reason for this behavior can be attributed to the lower competition for the sorption surface sites at lower concentration. At higher concentrations, the competition for the surface active sites will be high and consequently lower sorption rates are obtained. Similar phenomena have been observed in the adsorption of acid dyes on surfacant-modified bentonites (Baskaralingam et al. 2006; Özcan et al. 2005).

The kinetic data can also be analyzed by intraparticle diffusion kinetics model, formulated as (Weber and Morriss 1963),

$$q_t = k_i t^{1/2} + C \tag{6}$$

where k_i ($\mathrm{mg\,g^{-1}\,min^{-1/2}}$) is the intraparticle diffusion rate constant and C ($\mathrm{mg\,g^{-1}}$) is a constant. The values k_i, C and correlation coefficient calculated from the slope of the

Table 2 Comparison of the pseudo-first, pseudo-second-order and intraparticle diffusion adsorption constants at different initial dye concentrations

Adsorbent	C_0 (mg L^{-1})	Pseudo-first-order model				Pseudo-second-order model			Intraparticle diffusion model		
		q_e (exp) (mg g^{-1})	k_1 ($\times 10^{-2}$ min^{-1})	q_e (cal) (mg g^{-1})	r^2	k_2 ($\times 10^{-4}$ g mg^{-1} min^{-1}) (mg g^{-1})	q_e (cal)	r^2	k_i (mg g^{-1} min$^{-1/2}$)	C (mg g^{-1})	r^2
organo-attapulgite	250	117.25	2.324	52.27	0.8813	25.71	116.28	0.9996	4.334	75.39	0.9751
	300	138.13	2.153	86.99	0.9433	10.32	136.43	0.9980	7.917	58.14	0.9822
	350	154.13	2.676	114.25	0.9771	5.490	164.74	0.9976	12.094	42.46	0.9814

plots of q_t versus $t^{1/2}$ are shown in Table 3. It is found that the correlation coefficients for the intraparticle diffusion model are all above 0.97. The values of intercept give an idea about the boundary layer thickness, i.e., the larger the intercept, the greater the boundary layer effect (Kannan and Sundaram 2003). From Table 2, it is observed that the intercept C was not zero but large values, which decreases with increasing initial dye concentration for the organo-attapulgite. This result implies that boundary layer diffusion may be the rate-limiting step in the adsorption process for the organo-attapulgite (Özcan and Özcan 2004).

To determine the actual process involved in the present adsorption, mathematical treatments suggested by Boyd et al. (1947) and Reichenberg (1953) were used and were as follows:

$$F = 1 - \frac{6}{\pi^2} \sum_{1}^{\infty} \left(\frac{1}{n^2}\right) \exp[-n^2 Bt] \tag{7}$$

where F is the fractional attainment of equilibrium at time t and is obtained by the expression:

$$F = \frac{q_t}{q_\infty} \tag{8}$$

where q_t and q_∞ are amounts adsorbed after time t and after infinite time, respectively, and

$$B = \frac{\pi^2 D_i}{r_0^2} \tag{9}$$

where D_i is the effective diffusion coefficient of adsorbate in adsorbent phase; r_0 is the radius of the adsorbent particle, assumed to be spherical. In (7), B is defined by (9), and n is the index of summation that defines the infinite series solution.

For every observed value of F, corresponding values of Bt are obtained by applying (7). The Bt values were plotted against time as shown in Fig. 6. The linearity of this plot can be used to distinguish between film diffusion and intraparticle diffusion mechanism. If this plot is a straight line passing through origin, adsorption will be governed by an intraparticle diffusion mechanism, otherwise governed by film diffusion (Wang et al. 2006). It is obviously seen from Fig. 6 that the nature of the all graphs are not straight lines, indicating the film diffusion mechanism is the rate controlling step in a whole adsorption process. This result again confirms the mechanism of adsorption stated in intraparticle diffusion kinetic model studies.

3.5 Adsorption isotherms

Adsorption isotherms are important for the description of how molecules of adsorbate interact with adsorbent surface. Hence, the adsorption of CR onto organo-attapulgite

Table 3 Langmuir and Freundlich constants for the adsorption of CR onto organo-attapulgite at 30 °C

Adsorbent	Langmuir equation				Freundlich equation		
	q_m (mg g^{-1})	b (L mg^{-1})	R_L	r^2	K_f (mol$^{1-1/n}$ L$^{1/n}$ g^{-1})	n	r^2
organo-attapulgite	189.39	0.2907	0.00489	0.9999	114.74	10.68	0.9711

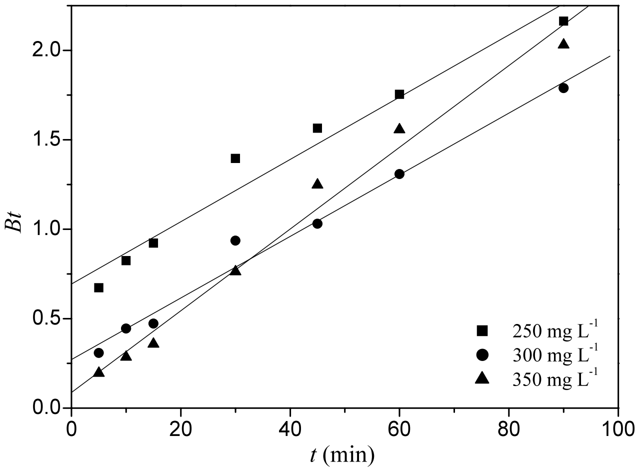

Fig. 6 *Bt* vs. *t* plots for the adsorption of CR onto organo-attapulgite at different initial dye concentrations

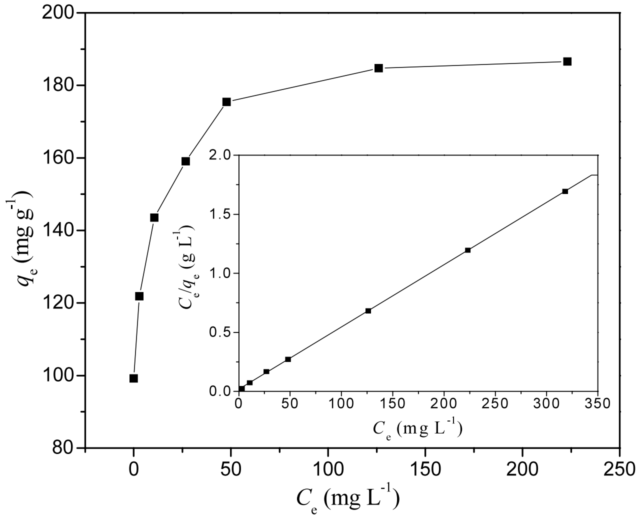

Fig. 7 Isotherm and Langmuir plot for the adsorption of CR onto organo-attapulgite

is determined as a function of equilibrium CR concentration (C_e) and the corresponding adsorption isotherm is plotted in Fig. 7. According to the classification of Giles et al. (1960), the isotherm seem to be of the L type, which indicates that it is connected with flat position of the adsorbate molecule toward the adsorbent surface and refers to the monolayer coverage.

The adsorption process is normally described by the Langmuir and the Freundlich isotherms. The Langmuir equation assumes that there is no interaction between the adsorbate molecules and that the sorption is localized in a monolayer. It is then assumes that once a dye molecule occupies a site, no further adsorption can take place at that site (Langmuir 1918). The Langmuir equation is commonly expressed as in the linear form:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{10}$$

where C_e is the equilibrium concentration of dye solution (mg L^{-1}), q_e is the equilibrium capacity of dye on the adsorbent (mg g^{-1}), q_m is the monolayer adsorption capacity of the adsorbent (mg g^{-1}), and b is the Langmuir adsorption constant (L mg^{-1}) and related to the free energy of adsorption.

The Freundlich adsorption model assumes that adsorption takes place on heterogeneous surfaces (Freundlich 1906). Its linear form can be written as:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{11}$$

where K_f and n (dimensionless) are the Freundlich adsorption isotherm constants, indicated the capacity and intensity of the adsorption, respectively.

Adsorption equations were obtained by experimental data with (10) and (11). The linear Langmuir and Freundlich plots for the adsorption of CR onto organo-attapulgite are obtained by plotting C_e/q_e vs. C_e (inserted in Fig. 7) and log q_e vs. log C_e (figure not shown), respectively. The isotherm constants and correlation coefficients were calculated and listed in Table 3. By comparing the correlation coefficients r^2, it can be deduced that the experimental equilibrium adsorption data are well described by the Langmuir equation compared to Freundlich model. This suggests the monolayer coverage of the surface of organo-attapulgite by CR molecules. The maximum adsorption capacity of 189.39 mg g^{-1} was found for organo-attapulgite. The high adsorption capacity in organo-attapulgite could be due to the large amount of surfactant on the surface of attapulgite particles, which could result in increasing amounts of positively charged sites on the surface of attapulgite and ultimately facilitates the attraction towards the negatively charged dye molecules. The monolayer adsorption was also reported for the CR adsorption onto coal-based mesoporous activated carbon (Lorenc-Grabowska and Gryglewicz 2007) and flyash (Rao and Rao 2006).

The essential characteristics of the Langmuir isotherm can be expressed by means of 'R_L', a dimensionless constant referred to as separation factor or equilibrium parameter R_L is defined by Al-Degs et al. (2000)

$$R_L = 1/(1 + bC_0) \tag{12}$$

where b is the Langmuir constant and C_0 is the initial dye concentration. The parameter indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). For CR, the R_L values were between 0 and 1.0, indicating that adsorption of CR onto the organo-attapulgite is favorable.

For Freundlich isotherm model, the n value between 1 and 10 indicates beneficial adsorption (Nir et al. 2000). For the adsorption of CR onto organo-attapulgite, the n value was above the favourable limit beneficial adsorption. This result is different with the above discussion on R_L value, which might be related with the difference of linearity of Langmuir and Freundlich adsorption isotherms.

3.6 Desorption of Congo red

Desorption studies can help elucidating the mechanism of an adsorption process. If the dye adsorbed onto the adsorbent can be desorbed by water, it can be said that the attachment of the dye onto the adsorbent is by weak bonds. If the strong bases, such as NaOH can desorbs the dye, it can be said that the attachment of the dye onto the adsorbent is by ion exchange (Mall et al. 2006). Hence, neutral distilled water was used in the elution of dyes from the organo-palygorskite followed by NaOH solution. Low desorption was obtained with neutral distilled water and the percentage of desorption for the organo-palygorskite was 13.67%. While in the case of 0.1 N NaOH solution, only 6.06% was obtained. The fact that the low desorption occurred with distilled water and NaOH solution suggests that adsorption of CR onto organo-palygorskite carries out significantly via a chemisorption mechanism. This result again substantiates the mechanism of adsorption mentioned in above studies.

4 Conclusions

In this study, palygorskite was modified by a cationic surfactant hexadecyltrimethylammonium bromide and the resulting sample was used as adsorbent for the removal of anionic dye CR from aqueous solution. The results show that the adsorption of CR onto organo-attapulgite was increased by increasing dye concentration and temperature, and by decreasing pH. The organo-attapulgite showed a higher adsorption capacity toward CR than natural attapulgite. The adsorption of CR onto organo-attapulgite was endothermic in nature.

Kinetic data of adsorption were well fitted by the pseudo-second-order kinetic model and the pseudo second-order rate constant, k_2, decreases with increasing initial dye concentration for the organo-attapulgite. Intraparticle diffusion study showed that film diffusion was operating during the process of the adsorption of CR onto organo-attapulgite. The equilibrium experimental data fit perfectly with the Langmuir isotherm. The maximum adsorption capacity was 189.39 $\mathrm{mg\,g^{-1}}$ for organo-attapulgite. In desorption studies, low desorption of dyes were obtained with water and NaOH solution. This indicates that chemisorption should be the major mode of dye removal by the organo-attapulgite. As a result it can be said that the surfactant-modified attapulgite is an effective adsorbent for the removal of Congo red from aqueous solution.

References

Aksu, Z.: Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of lead(II) ions onto Chlorella vulgaris. Process Biochem. **38**(1), 89–99 (2002)

Al-Degs, Y., Khraisheh, M.A.M., Allen, S.J., et al.: Effect of carbon surface chemistry on the removal of reactive dyes from textile effluent. Water Res. **34**(3), 927–935 (2000)

Al-Futaisi, A., Jamrah, A., Al-Rawas, A., et al.: Adsorption capacity and mineralogical and physico-chemical characteristics of Shuwaymiyah palygorskite (Oman). Environ. Geol. **51**(8), 1317–1327 (2007)

Alkan, M., Demirbaş, Ö., Çelikçapa, S., Doğan, M.: Sorption of acid red 57 from aqueous solution onto sepiolite. J. Hazard. Mater. **116**(1–2), 135–145 (2004)

Alkan, M., Çelikçapa, S., Demirbaş, Ö.: Removal of reactive blue 221 and acid blue 62 anionic dyes from aqueous solutions by sepiolite. Dyes Pigments **65**(3), 251–259 (2005)

Armağan, B., Turan, M., Çelik, M.S.: Equilibrium studies on the adsorption of reactive azodyes into zeolite. Desalination **170**(1), 33–39 (2004)

Bache, B.W.: The measurement of cation exchange capacity of soils. J. Sci. Food Agric. **27**, 273–280 (1976)

Baskaralingam, P., Pulikesi, M., Elango, D., Ramamurthi, V., Sivanesan, S.: Adsorption of acid dye onto organobentonite. J. Hazard. Mater. **128**(2–3), 138–144 (2006)

Boyd, G.E., Adamson, A.W., Meyers, L.S.: The exchange adsorption of ions from aqueous solution by organic zeolites. II: Kinetics. J. Am. Chem. Soc. **69**, 2836–2848 (1947)

Chen, H., Wang, A.Q.: Kinetic and isothermal studies of lead ions adsorption onto palygorskite clay. J. Colloid Interface Sci. **307**(2), 309–316 (2007)

Chen, H., Zhao, Y.G., Wang, A.Q.: Removal of Cu(II) from aqueous solution by adsorption onto acid-activated palygorskite. J. Hazard. Mater. **149**(2), 346–354 (2007)

Chiou, M.S., Ho, P., Ho, Y., Li, H.Y.: Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads. Dyes Pigments **60**(1), 69–84 (2004)

Czímerová, A., Bujdák, J., Gáplovský, A.: The aggregation of thionine and methylene blue dye in smectite dispersion. Colloids Surf. A: Physicochem. Eng. Aspects **243**(1–3), 89–96 (2004)

Freundlich, H.M.F.: Über die adsorption in lösungen. Z. Phys. Chem. **57**, 385–470 (1906)

Frost, R.L., Locos, O.B., Ruan, H., Kloprogge, J.T.: Near-infrared and mid-infrared spectroscopic study of sepiolites and palygorskites. Vib. Spectrosc. **27**(1), 1–13 (2001)

Galan, E.: Properties and applications of palygorskite-sepiolite clays. Clay Miner. **31**(4), 443–453 (1996)

Giles, C.H., MacEwan, S.N., Nakhwa, S.N., Smith, D.: Studies in adsorption. Part XI. A system of classification of solution adsorption isotherm, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface area in solids. J. Chem. Soc. **3**, 3973–3993 (1960)

Gong, R., Ding, Y., Li, M., Yang, C., Liu, H., Sun, Y.: Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution. Dyes Pigments **64**(3), 187–192 (2005)

Gupta, G.S., Prasad, G., Singh, V.N.: Removal of chrome dye from aqueous solutions by mixed adsorbents: Fly ash and coal. Water Res. **24**(1), 45–50 (1990)

Halliday, P.J., Beszedits, S.: Color removal from textile mill wastewaters. Can. Text. J. **103**, 78–84 (1986)

Harris, R.G., Wells, J.D., Johnson, B.B.: Selective adsorption of dyes and other organic molecules to kaolinite and oxide surfaces. Colloids Surf. A: Physicochem. Eng. Aspects **180**(1–2), 131–140 (2001)

Ho, Y.S., McKay, G.: Pseudo-second order model for sorption processes. Process Biochem. **34**(5), 451–465 (1999)

Hu, Q.H., Qiao, S.Z., Haghseresht, F., Wilson, M.A., Lu, G.Q.: Adsorption study for removal of basic red dye using bentonite. Ind. Eng. Chem. Res. **45**(2), 733–738 (2006)

Huang, J.H., Liu, Y.F., Jin, Q.Z., et al.: Adsorption studies of a water soluble dye, Reactive Red MF-3B, using sonication-surfactant-modified attapulgite clay. J. Hazard. Mater. **143**(1–2), 541–548 (2007)

Kannan, N., Sundaram, M.M.: Kinetics and mechanism of removal of methylene blue by adsorption on various carbons-a comparative study. Dyes Pigments **51**(1), 25–40 (2003)

Lagergren, S.: About the theory of so-called adsorption of soluble substances. Kungliga Svenska Vetensk. Handl. **24**(4), 1–39 (1898)

Langmuir, I.: The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc. **40**(9), 1361–1403 (1918)

Lorenc-Grabowska, E., Gryglewicz, G.: Adsorption characteristics of Congo red on coal-based mesoporous activated carbon. Dyes Pigments **74**(1), 34–40 (2007)

Mall, I.D., Srivastava, V.C., Kumar, G.V.A., Mishra, I.M.: Characterization and utilization of mesoporous fertilizer plant waste carbon for adsorptive removal of dyes from aqueous solution. Colloids Surf. A: Physicochem. Eng. Aspects **278**(1–3), 175–187 (2006)

Mckay, G., Otterburn, M.S., Aga, J.A.: Fuller's earth and fired clay as adsorbents for dyestuffs. Water Air Soil Pollut. **24**(3), 307–322 (1985)

Neamtu, M., Yediler, A., Siminiceanu, I., Macoveanu, M., Kellrup, A.: Decolorization of disperse red 354 azo dye in water by several oxidation processes-a comparative study. Dyes Pigments **60**(1), 61–68 (2004)

Nir, S., Undabeytia, T., Yaron-Marcovich, D., El-Nahhal, Y., et al.: Optimization of adsorption of hydrophobic herbicides on montmorillonite preadsorbed by monovalent organic cations: interaction between phenyl rings. Environ. Sci. Technol. **34**(7), 1269–1274 (2000)

Ogawa, M., Kawai, R., Kuroda, K.: Adsorption and aggregation of a cationic cyanine dye on smectites. J. Phys. Chem. **100**(40), 16218–16221 (1996)

Özcan, A.S., Erdem, B., Özcan, A.: Adsorption of Acid Blue 193 from aqueous solutions onto BTMA-bentonite. Colloids Surf. A: Physicochem. Eng. Aspects **266**(1–3), 73–81 (2005)

Özcan, A.S., Tetik, S., Özcan, A.: Adsorption of acid dyes from aqueous solutions onto sepiolite. Sep. Sci. Technol. **39**(2), 301–320 (2004)

Özcan, A., Öncü, E.M., Özcan, A.S.: Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite. Colloids Surf. A: Physicochem. Eng. Aspects **277**(1–3), 90–97 (2006)

Özcan, A.S., Özcan, A.: Adsorption of acid dyes from aqueous solutions onto acid-activated bentonite. J. Colloid Interface Sci. **276**(1), 39–46 (2004)

de Paiva, L.B., Morales, A.R., Valenzuela Díaz, F.R.: Organoclays: Properties, preparation and applications. Appl. Clay Sci. **42**(1–2), 8–24 (2008)

Patil, S.S., Shinde, V.M.: Biodegradation studies of aniline and nitrobenzene in aniline plant wastewater by gas chromatography. Environ. Sci. Technol. **22**(10), 1160–1165 (1988)

Pelekani, C., Snoeyink, V.L.: A kinetic and equilibrium study of competitive adsorption between atrazine and Congo red dye on activated carbon: the importance of pore size distribution. Carbon **39**(1), 25–37 (2001)

Rao, K.C.L.N., Ashutosh, K.K.: Color removal from a dyestuff industry effluent using activated carbon. Indian J. Chem. Technol. **1**, 13–19 (1994)

Rao, V.V.B., Rao, S.R.M.: Adsorption studies on treatment of textile dyeing industrial effluent by flyash. Chem. Eng. J. **116**(1), 77–84 (2006)

Reichenberg, D.: Properties of ion exchange resins in relation to their structure. III. Kinetics of exchange. J. Am. Chem. Soc. **75**(3), 589–597 (1953)

Seshadri, S., Bishop, P.L., Agha, A.M.: Anaerobic/aerobic treatment of selected azo dyes in wastewater. Waste Manag. **15**(2), 127–137 (1994)

Tahir, S.S., Rauf, N.: Removal of a cationic dye from aqueous solutions by adsorption onto bentonite clay. Chemosphere **63**(11), 1842–1848 (2006)

Wahi, R.K., Yu, W.W., Liu, Y.P., et al.: Photodegradation of Congo Red catalyzed by nanosized TiO_2. J. Mol. Catal. A: Chem. **242**(1–2), 48–56 (2005)

Wang, C.C., Juang, L.C., Hsu, T.C., Lee, C.K., Lee, J.F., Huang, F.C.: Adsorption of basic dyes onto montmorillonite. J. Colloid Interface Sci. **273**(1), 80–86 (2004)

Wang, S., Boyjoo, Y., Choueib, A.: A comparative study of dye removal using fly ash treated by different methods. Chemosphere **60**(10), 1401–1407 (2005)

Wang, S., Li, H., Xu, L.: Application of zeolite MCM-22 for basic dye removal from wastewater. J. Colloid Interface Sci. **295**(1), 71–78 (2006)

Weber, W.J. Jr., Morriss, J.C.: Kinetics of adsorption on carbon from solution. J. Sanit. Eng. Div. Am. Soc. Civ. Eng. **89**, 31–60 (1963)